云 南 植 物 研 究 2008, 30 (2): 239～242
Acta Botanica Yunnanica DOI: 10.3724/SP. J. 1143. 2008. 07175

旋花茄新鲜果实中的三个甾体皂苷

滕希峰[1,2], 张颖君[1*], 杨崇仁[1*]

(1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650204;
2 中国科学院研究生院, 北京 100049)

摘要: 从茄科食用植物旋花茄 (*Solanum spirale*) 的新鲜果实中分离得到3个化合物, 其中一个为新成分, 经现代波谱学方法鉴定为26-*O*-β-D-葡萄吡喃糖基-(25*R*)-呋甾-3β, 22ξ, 26-三醇-5-烯-3-*O*-α-L-鼠李吡喃糖基-(1-2)-[3-*O*-(3-*O*-乙酰基)-α-L-鼠李吡喃糖基-(1-4)]-β-D-葡萄吡喃糖苷 (**1**)。2个已知化合物分别为26-*O*-β-D-葡萄吡喃糖基-(25*R*)-呋甾-22ξ-甲氧基-3β, 26-二醇-5-烯-3-*O*-α-L-鼠李吡喃糖基-(1-2)-β-D-葡萄吡喃糖苷 (**2**) 和26-*O*-β-D-葡萄吡喃糖基-(25*R*)-呋甾-3β, 22ξ, 26-三醇-5-烯-3-*O*-α-L-鼠李吡喃糖基-(1-2)-[α-L-鼠李吡喃糖基-(1-4)]-β-D-葡萄吡喃糖苷 (protodioscin) (**3**), 均为首次从该植物中分离得到。

关键词: 茄科; 旋花茄; 甾体皂苷

中图分类号: Q 946 **文献标识码**: A **文章编号**: 0253-2700 (2008) 02-239-04

Three Steroidal Glycosides from the Fresh Fruits of *Solanum spirale* (Solanaceae)

TENG Xi-Feng[1,2], ZHANG Ying-Jun[1*], YANG Chong-Ren[1*]

(1 *State Key Laboratory of Phytochemistry and Plant Resources in West China*, *Kunming Institute of Botany*,
Chinese Academy of Sciences, Kunming 650204, China;
2 *Graduate University of Chinese Academy of Sciences*, Beijing 100049, China)

Abstract: One new steroidal glycoside, 26-*O*-β-D-glucopyranosyl-(25*R*)-furost-3β, 22ξ, 26-triol-5-ene-3-α-L-rhamnopyranosyl-(1-2)-[3-*O*-(3-*O*-acetyl)-α-L-rhamnopyranosyl-(1-4)]-β-D-glucopyranoside (**1**) were isolated from the fresh fruits of the edible plant *Solanum spirale* Roxb., together with two known ones, 26-*O*-β-D-glucopyranosyl-(25*R*)-furost-22ξ-methoxyl-3β, 26-diol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-β-D-glucopyranoside (**2**) and 26-*O*-β-D-glucopyranosyl-(25*R*)-furost-3β, 22ξ, 26-triol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-[α-L-rhamnopyranosyl-(1-4)]-β-D-glucopyranoside (protodioscin) (**3**). Their structures were elucidated by spectroscopic methods, especially 2D NMR. The known compounds **2-3** were isolated from the title plant for the first time.

Key words: Solanaceae; *Solanum spirale*; Steriodal glycosides

Solanum spirale Roxb. is distributed mainly in Yunnan, Guizhou, Guangxi, and Hunan provinces of China, India, Bengal, Burma, Thailand, and Vietnam. In China, the tender leaves and fruits are edible and have been used as a wild vegetable by Dai people (Kunming Institute of Botany, Chinese Academy Sciences, 1979). The leaves are also reported to have the effects on killing intestinal worms and the roots are used as a narcotic and diuretic in India. And the Vietnamese use the ripe fruits as vegetable and the leaves as folk medicine against beriberi and swollen stomach (Quyen *et al*., 1987).

Three compounds, tomatidenol, 15α-hydroxytomatidenol and yamogenin, were isolated from the leaves of

---

[*] Author for correspondence; E-mail: zhangyj@mail.kib.ac.cn, cryang@mail.kib.ac.cn; Tel: +86-871-5223235

Received date: 2007-08-27, Accepted date: 2007-11-29

作者简介: 滕希峰 (1977-) 男, 在读博士研究生, 主要从事中药资源与化学研究。

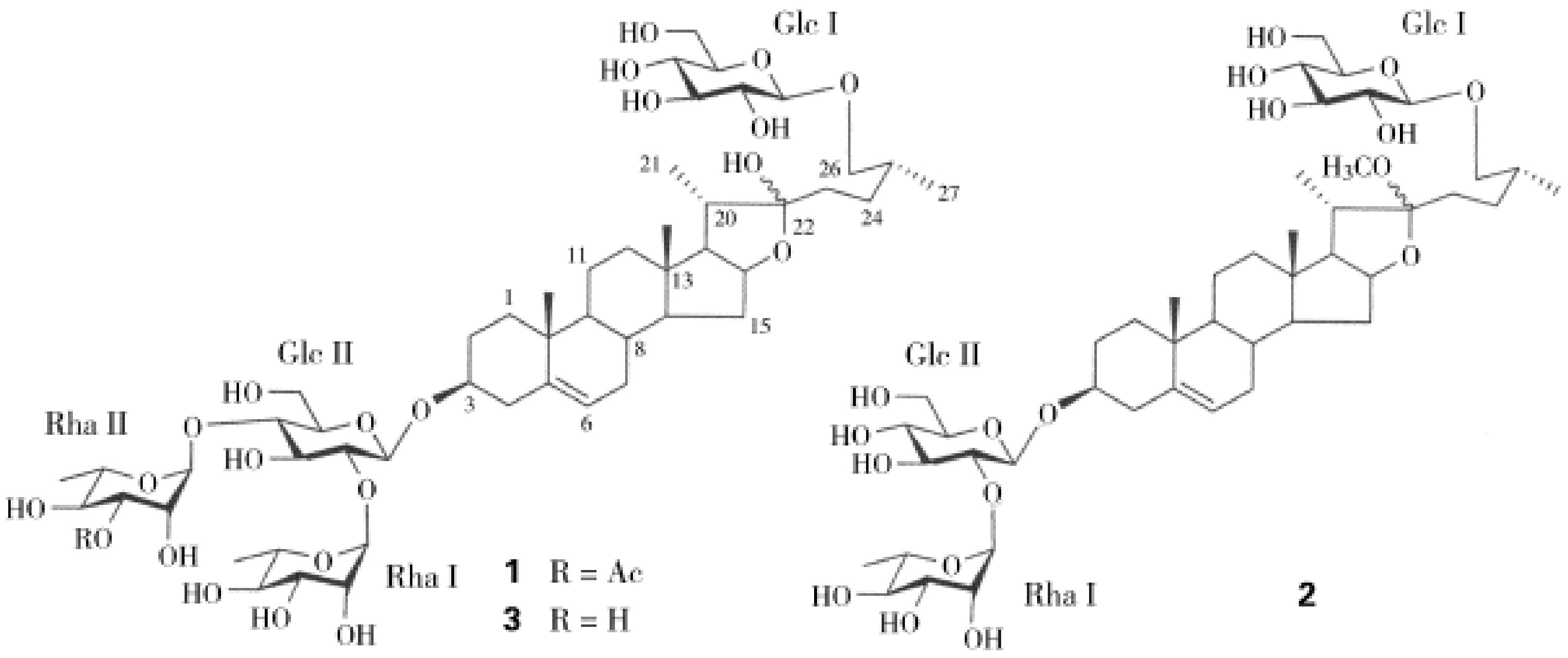

Fig. 1 Structures of compounds **1 - 3**

S. spirale (Quyen *et al.*, 1987), while etioline, solaspiralidine and 3-*O*-(β-glucopyranosyl)-etioline were reported from the roots (Ripperger, 1996). As a part of our phytochemical investigation on edible plant in West China, three steroidal glycosides (**1 - 3**) were identified from the fresh fruits of this plant for the first time (Fig. 1). Of them, **1** is a new compound. Two known compounds were determined to be 26-*O*-β-D-glucopyranosyl-(25R)-furost-22ξ-methoxyl-3β, 26-diol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-β-D-glucopyranoside (**2**) (Silva *et al.*, 1998), and 26-*O*-β-D-glucopyranosyl-(25*R*)-furost-3β, 22ξ, 26-triol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-[α-L-rhamnopyranosyl-(1-4)]-β-D-glucopyranoside (protodioscin) (**3**) (Watanabe *et al.*, 1983), respectively, by comparison of their NMR data with the reported literature values.

Compound **1** was obtained as white amorphous powder and showed a positive reaction with the Ehrlich reagent, suggesting that **1** was a furostanol glycoside. Its molecular formula was assigned as $C_{53}H_{86}O_{23}$ on the basis of HRFABMS *m/z* 1089.5457 $[M-H]^-$ (calcd. for $C_{53}H_{85}O_{23}$: 1089.5481). The ^1H NMR spectrum displayed four methyl signals of a typical steroidal skeleton at [δ 0.88, 1.04 (each 3H, s), 0.97 (3H, d, *J* = 6.2 Hz), 1.32 (3H, d, *J* = 7.1 Hz)] as well as four anomeric proton signals at δ 4.80 (1H, d, *J* = 7.6 Hz, GlcII H - 1), 5.85 (1H, s, RhaII H - 1), 4.94 (1H, d, *J* = 7.2 Hz, GlcI H - 1), and 6.39 (1H, br s, RhaI H - 1)]. These NMR features were closely related to those of protodioscin (**3**), except for the appearance of additional signals rising from an acetyl group: an isolated methyl proton signals at δ 1.94 (3H, s, $OCOCH_3$), a carbonyl carbon at δ 170.8, and a methyl carbon at δ 20.9. Comparing to those of **3**, the downfield shift of C - 3 of RhaII by 1.4 ppm together with the upfield shift of C - 2 and C - 4 by 0.8 and 1.3 ppm, respectively, suggested that the acetyl group was linked to C - 3 of RhaII in **1**. This was further supported by the HMBC correlations of H - 3 (δ 4.82) of RhaII with the acetyl carbonyl carbon at δ 170.8. Other HMBC correlations (Fig. 2) confirmed the structure of **1** as 26-*O*-β-D-glucopyranosyl-(25 *R*)-furost-3β, 22ξ, 26-triol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-[3-*O*-(3-*O*-acetyl)-α-L-rhamnopyranosyl-(1-4)]-β-D-glucopyranoside.

Experimental section

General Experimental Procedures Optical rotation was measured on a HORIBA SEPA-3000 automatic digital polarimeter. The NMR spectra were recorded in pyridine-d_5 on a Brucker AM-400 and DRX-500 instruments with TMS as internal standard. FABMS data were recorded on a VG Auto Spec3000 spectrometer and the HRESIMS on API Qstar Pulsar spectrometer. Si gel (200 - 300 mesh) for column chromatography (CC) and GF254 for TLC were obtained from the Qingdao Marine Chemical Factory, Qingdao, People's Republic of China. Rp-8 (40 - 63 μm) for CC was from Merck Corporation.

Plant Material The fresh fruits of *S. spirale* were collected

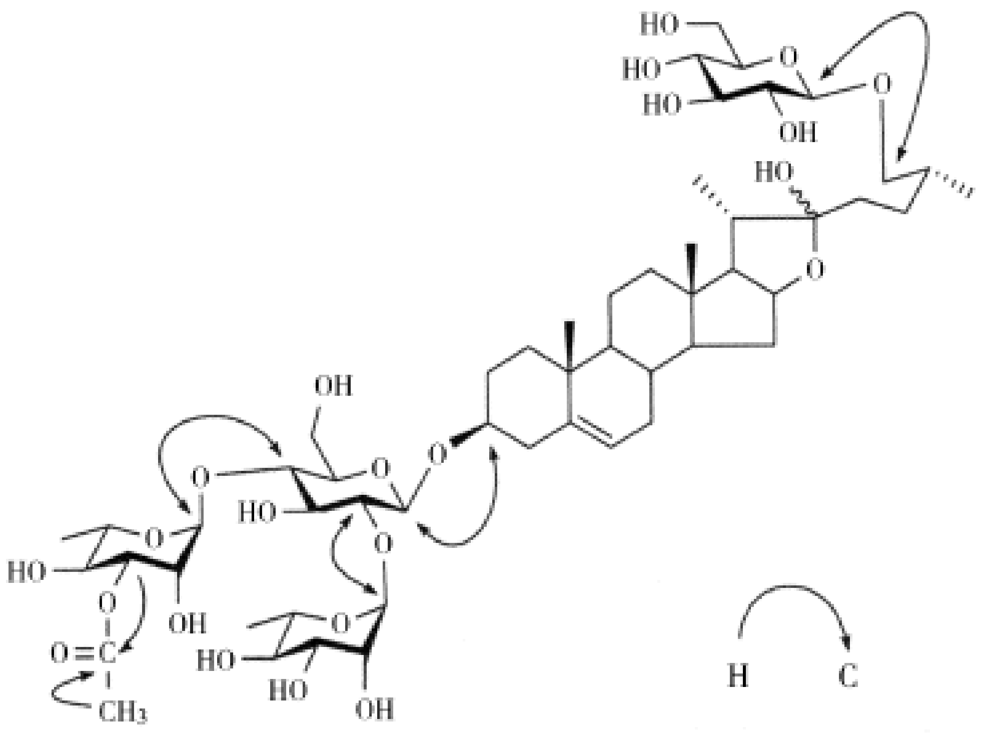

Fig . 2 Key HMBC correlations of **1**

from Xishuangbanna, Yunnan, and identified by Prof. C. R. Yang, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation The fresh fruits (540 g) of *S. spirale* were extracted with MeOH (800 ml × 3) under reflux 3 times. After removal of the solvent under reduced pressure, the concentrate was suspended into H_2O and partioned successively with petroleum ether, AcOEt, and n-BuOH. The n-BuOH fraction (25 g) was subjected to column chromatography on silica gel, eluting with $CHCl_3$-MeOH-H_2O (7∶3∶0.5) to give five fractions (Fr. 1-5), Fr. 3 was subjected to reverse phase RP-8 column eluting with MeOH-H_2O (7∶3) to afford **1** (35 mg), **2** (60 mg) and **3** (12 mg).

Table 1 ^{13}C NMR spectral data of compounds **1 - 3**

No.	**1**	**2**	**3**	sugar	**1**	**2**	**3**
1	37.6	37.6	37.5	GlcI-1	100.5	100.2	100.4
2	30.1	30.0	30.0	2	78.0	79.1	77.9
3	78.4	78.7	78.5	3	78.0	78.5	78.0
4	39.1	39.0	39.5	4	78.3	71.9	78.2
5	141.0	141.0	140.9	5	77.0	78.7	77.0
6	121.9	121.9	121.9	6	61.4	63.0	61.6
7	32.5	32.5	32.4	RhaI-1	102.1	102.1	102.0
8	31.8	31.8	31.8	2	72.6	72.4	72.6
9	50.5	50.4	50.5	3	72.8	72.8	72.9
10	37.2	37.2	37.2	4	74.2	74.2	74.1
11	21.2	21.1	21.1	5	69.6	69.5	69.6
12	40.0	39.8	40.0	6	18.8	18.7	18.7
13	40.9	40.6	40.9	RhaII-1	103.0		102.9
14	56.7	56.7	56.2	2	71.8		72.6
15	32.6	32.5	32.6	3	74.2		72.8
16	81.2	81.4	81.3	3-O-$\underline{CO}CH_3$	170.8		
17	63.9	64.3	63.8	3-O-CO$\underline{CH_3}$	20.9		
18	16.6	16.4	16.5	4	72.6		73.9
19	19.5	19.5	19.5	5	70.5		70.5
20	40.8	40.9	40.8	6	18.6		18.5
21	16.5	16.3	16.4	GlcII-1	105.0	105.0	105.0
22	110.8	112.7	110.8	2	75.2	75.2	75.3
23	37.2	30.9	37.2	3	78.7	78.7	78.6
24	28.4	28.3	28.2	4	71.9	71.9	71.8
25	34.5	34.3	34.5	5	78.5	78.5	78.5
26	75.3	75.2	75.4	6	62.8	63.0	62.9
27	17.6	17.2	17.5				
OMe		47.4					

26-*O*-β-D-glucopyranosyl-(25*R*)-furost-3β, 22ξ, 26-triol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-[3-*O*-(3-O-acetyl)-α-L-rhamnopyranosyl-(1-4)]-β-D-glucopyranoside (**1**), $C_{53}H_{86}O_{23}$, White amorphous powder, $[\alpha]_D^{22}$ -51.6 (c 0.18, MeOH). FABMS (negative ion mode), *m/z* 1089 $[M-H]^-$, 943 $[M-146-H]^-$, 901 $[M-146-42-H]^-$, 739 $[M-146-42-162-H]^-$, HRFABMS (negative ion mode): *m/z* 1089.5457 $[M-H]^-$ (calcd. $C_{53}H_{85}O_{23}$ for 1089.5481); ^{1}H NMR (pyridine-d_5, 400 MHz) δ 0.88 (3H, s, H-18), 0.97 (3H, d, *J* = 6.2 Hz, H-27), 1.04 (3H, s, H-19), 1.32 (3H, d, *J* = 7.1 Hz, H-21), 1.61 (3H, d, *J* = 5.5 Hz, RhaII H-6). 1.75 (3H, d, *J* = 5.5 Hz, RhaI H-6), 1.94 (3H, s, RhaII 3-O-CO$\underline{CH_3}$), 2.20 (1H, m, H-20), 2.73 (1H, m, H-4), 4.80 (1H, d, *J* = 7.6 Hz, GlcII H-1), 4.82 (1H, m, RhaII H-3), 4.94 (1H, d, *J* = 7.2 Hz, GlcI H-1), 4.95 (1H, m, H-16), 5.29 (1H, br s, H-6), 5.85 (1H, br s, RhaII H-1), 6.39 (1H, br s, RhaI H-1), ^{13}C-NMR (pyridine-d_5, 100 MHz): see table 1.

26-*O*-β-D-glucopyranosyl-(25*R*)-furost-22ξ-methoxyl-3β, 26-diol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-β-D-glucopyranoside (**2**), $C_{46}H_{76}O_{18}$, White amorphous powder, FAB-MS (negative ion mode) *m/z* 915 $[M-H]^-$, 769 $[M-146-H]^-$; ^{13}C NMR (pyridine-d_5, 100 MHz): see table 1.

26-*O*-β-D-glucopyranosyl-(25*R*)-furost-3β, 22ξ, 26-triol-5-ene-3-*O*-α-L-rhamnopyranosyl-(1-2)-[α-L-rhamnopyranosyl-(1-4)]-β-D-glucopyranoside (protodioscin) (**3**), $C_{51}H_{84}O_{22}$, White amorphous powder, FAB-MS (negative ion mode) *m/z* 1047 $[M-H]^-$, 901 $[M-146-H]^-$, 755 $[M-146-146-H]^-$, 593 $[M-146-146-162-H]^-$, 431 $[M-146-146-162-162-H]^-$; ^{13}C NMR (pyridine-d_5, 100 MHz): see table 1.

Acknowledgment: The authors thank the staffs of the analytical group at State Key Labrotory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, for measuring the spectral data.

References:

Kunming Institute of Botany, Chinese Academy Sciences, 1979. Flora of Yunnannica Vol. 2 [M]. Beijing: Science Press, 566—568

Quyen LT, Khoi NH, Suong NN *et al.*, 1987. Steroid alkaloids and yamogenin from *Solanum spirale* [J]. *Plant Medica*, **52** (3): 292—293

Ripperger H, 1996. Steroidal alkaloids from roots of *Solanum spirale* [J]. *Phytochmistry*, **43** (3): 705—707

Silva BP, Bernardo RR, Parente JP, 1998. New furostanol glycosides from *Costus spicatus* [J]. *Fitoterapia*, **69** (6): 528—532

Watanabe Y, Sanada S, Ida Y *et al.*, 1983. Comparative studies on the constituents of *Ophiopogonis* tuber and its congeners. 1. studies of the constituents of the subterranean part of Liriope platyphylla Wang et Tang [J]. *Chem Pharm Bull*, **31** (6): 1980—1990